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# RCA

LB-922

## CONTINUOUS-PROCESS APPARATUS

### FOR GROWING

### SINGLE-CRYSTAL GERMANIUM

# RADIO CORPORATION OF AMERICA
# RCA LABORATORIES DIVISION
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## Continuous-Process Apparatus for Growing

## Single-Crystal Germanium

Approved

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# Continuous-Process Apparatus for Growing Single-Crystal Germanium

## Introduction

The development and testing of apparatus for growing continuous-process single-crystal germanium of controlled and uniform electrical resistivity are described in this bulletin. This continuous process, using the Czochralski technique, involves the simultaneous feed-in of poly-crystalline material and the withdrawal of single-crystalline material. A mathematical expression relating pertinent parameters to the electrical resistivity of the single crystal is also given. With this expression as a guide, the technique described lends itself to the production of crystals which are of a predetermined and relatively uniform resistivity from one end to the other.

## General Considerations

When in early transistor work with germanium and silicon it became evident that single-crystal material must be used for best results, the Czochralski[1] method became the popular technique for producing this material. By this method crystals are grown from a melt by touching a single-crystal seed to the liquid surface and slowly withdrawing it as new lattice layers are added to it by germanium freezing out from the melt. One type of apparatus for growing single crystals by this method has been described in an earlier bulletin.[2]

Single crystals produced in this and similar apparatus provide acceptable material for germanium transistors and rectifiers. These crystals do, however, suffer from the limitation that they vary in resistivity from one end to the other. Since, in general, the impurities have lower solubilities in solid than in liquid germanium, the concentration of these impurities in the melt and the rate at which they enter the crystal lattice increase as more and more



Fig. I – Variation in resistivity along length of single crystal grown by original Czochralski method.

[1](a) J. Czochralski, *Z. Physik. Chem.*, Vol. 92, p. 219 (1918).

(b) G. K. Teal and J. B. Little, *Phys. Rev.*, Vol. 78, p. 647 (1950).

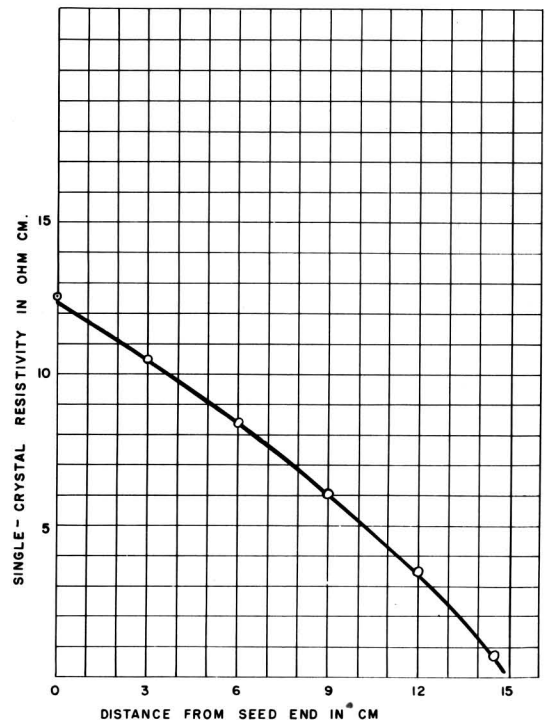[2]LB-892, *Preparation of Single Crystals of Germanium and Silicon.*

of the melt is incorporated into the growing crystals. The end of the crystal first drawn from the melt will, therefore, possess a lower impurity concentration and a higher electrical resistivity than will the end drawn out last. A curve indicating the typical resistivity variation obtained is shown in Fig. 1.

Since in the fabrication of semiconductor devices it is important that as little as possible variation in material exist from unit to unit, it follows that crystals more uniform in resistivity from one end to the other are desirable. An apparatus for growing single crystals of this type has been developed and is described in this bulletin.

## Apparatus and Procedure

The apparatus which has been constructed and put into operation is of the continuous-process type and is shown in Figs. 2 and 3. It consists of a Vycor furnace tube 24 inches x $2\frac{1}{2}$ inches, with two 18-inch x $1\frac{1}{2}$-inch side arms supported in a W & B No. 30 firebrick furnace and heated by Globars. In the furnace tube below the vertically placed side arms, a graphite boat is positioned so that one of the two channel-connected pot-holes is centered with the axis of each side arm. A germanium charge of 250 grams is placed in the graphite boat. A properly oriented single-crystal seed is clamped in a stainless-steel holder which extends through a brass bushing closing the top of one of the Vycor-tube side-arms. The threaded cylindrical rod which forms the upper part of the holder passes through a mechanism for lifting and turning the seed holder.

Suspended above the second pot-hole in the graphite boat is a rod of polycrystalline germainum which is clamped into a stainless-steel holder extending through a bushing at the top of the second Vycor-tube side-arm. This holder, after passing through a second guide bushing, is attached by means of a wire cable to a lowering mechanism. The open ends of the Vycor furnace tube are closed by brass caps provided with quartz windows for observation purposes. The brass caps are also provided with gas inlets and holes for a thermocouple and an auxiliary heater.
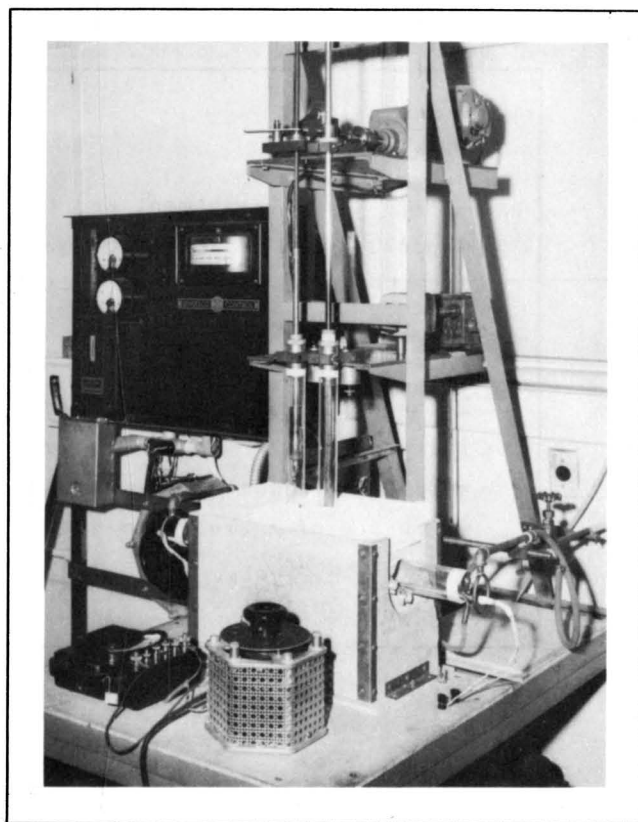


Fig. 2 – Photograph of apparatus for continuous-process production of single-crystal germanium.

With argon mixed with about 10 per cent hydrogen flowing through the system, the germanium is melted by heat supplied through the Globars. The molten germanium is elevated to a temperature of about 1000 degrees C and maintained at this temperature for about 5 minutes. The feed-in mechanism is then started to lower the polycrystalline rod of germanium into the melt at a rate of about one millimeter per minute. A Wheelco temperature controller, equipped with Xactline anticipator and means for high-low rather than on-off regulation, is set to lower and maintain the temperature of the germanium at a value just above the melting point, 936 degrees C. Temperature information is supplied to the regulator by a thermocouple enclosed in Vycor tubing and inserted into the the end of the graphite boat. To supply extr heat for melting germanium from the feed-in rod, an auxiliary nichrome heater, enclosed in Vycor tubing, is inserted into the graphite boat below the feed-in pot-hole. The seed, which has been preheated by holding it about 2 millimeters above the surface of the melt, is brough

into contact with the liquid germanium and withdrawal begun at a rate of 1 millimeter per minute and with the seed rotated at 60 rpm. Final adjustment of temperature is made to cause the single crystal to grow at a desired diameter (usually 2 centimeters when germanium is removed from the melt at the same rate as at which it is fed in).
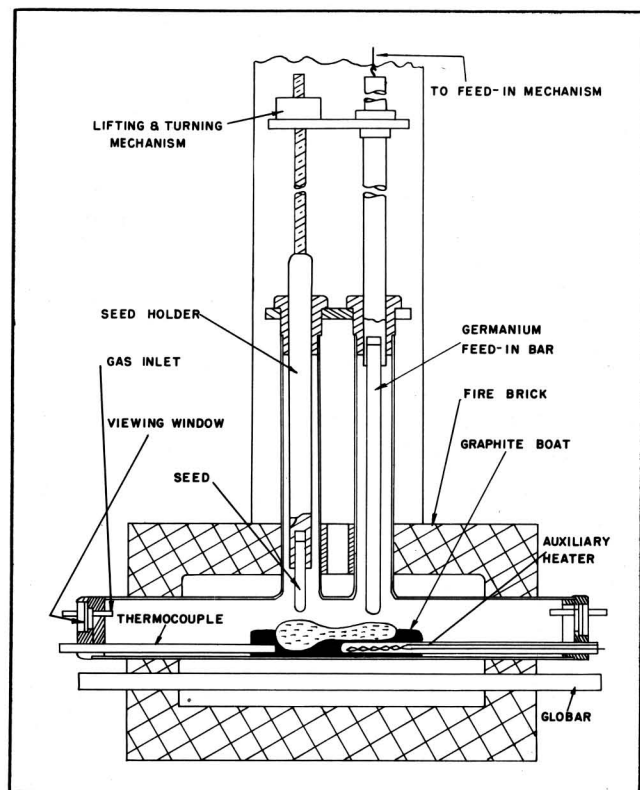


Fig. 3 – Cross-section of furnace shown in Fig. 2.

## Control of Resistivity of the Single-Crystal Material

The apparatus and procedure described above can be used to grow crystals uniform in resistivity from one end to the other. If, for instance, n-type single-crystal is desired, the proper impurity concentration is introduced into the melt to cause donors to enter the crystal lattice under equilibrium growing conditions at a rate which produces the required donor concentration in the single crystal produced. To keep the impurity concentration in the melt constant, the feed-in material is chosen to cause the introduction into the melt of donors at the same rate as they enter the growing crystal.

To make possible control of the factors referred to above for the purpose of pre-determining the resistivity of single-crystal material and for evaluating the effects of lack of perfect control under practical operating conditions, a mathematical expression relating pertinent parameters to the electrical resistivity of the single crystal must be derived.

For this purpose let us assume that in producing single crystals of predetermined resistivity we limit ourselves (as is for practical purpose desirable) to the use of intrinsic germanium for raw materials, and to the use of one impurity or "doping" element of the acceptor type for the preparation of p-type material and one "doping" element of the donor type for the preparation of n-type material. Let us further assume that the contribution of the thermally-produced carrier to the conductivity of the germanium is negligible. It follows then, since each impurity atom supplies one current carrier to the crystal lattice, that the conductivity of the single-crystal material formed is directly proportional to the density, $n_c$, of the impurity included in the lattice. Considering also that this density is directly proportional to the density, $n$, of impurity in the melt and that the factors of proportionality can be determined for any particular impurity used, it follows that knowledge of $n$ as a function of time will permit the calculation of the resistivity and the variation in resistivity from one end to the other of single crystals produced.

At the start of crystal formation and of feed-in, $n = N_o/V$ where $N_o$ is the number of impurity atoms originally introduced into the volume $V$ of the melt. If, however, the rate at which the impurity atoms leave the melt at the point of crystal growth differs from the rate at which they are introduced at the point of feed-in, the total number of impurities in the melt, $N$, will change with time so that, after an increment of time $\Delta t$,

$$N = N_o + (A_f v_f n_f - A_c v_c n_c)\Delta t \qquad (1)$$

or

$$\Delta N = (A_f v_f n_f - A_c v_c n_c)\Delta t \qquad (2)$$

where $A_f$, $v_f$, $n_f$, and $A_c$, $v_c$, $n_c$ are the cross-section area, the feed-in rate or growth rate, and the density of impurity atoms of the feed-in rod and of the single crystal grown, respectively.

If the operating conditions are arranged so that $A_c = A_f$ and $v_c = v_f$, and if the symbol $V_r$ is substituted for the equal $A_f v_f$ and $A_c v_c$, then

$$\Delta N = (V_r n_f - V_r n_o)\Delta t \tag{3}$$

or since

$$\Delta n = \frac{\Delta N}{V}$$

$$\frac{\Delta n}{\Delta t} = \frac{V_r n_f}{V} - \frac{V_r n_c}{V} \tag{4}$$

and since $n_c = kn$, where $k$ is the distribution coefficient of the impurity used,

$$\frac{dn}{dt} + \frac{V_r kn}{V} = \frac{V_r n_f}{V} \tag{5}$$

A solution of this differential equation with initial conditions taken into account gives

$$n = \left(n_o - \frac{n_f}{k}\right)e^{-\frac{V_r kt}{V}} + \frac{n_f}{k} \tag{6}$$

where $n_o$ = density of impurity atoms in melt at $t = 0$.

Since resistivity is inversely proportional to density of impurity atoms, the performance of the requisite algebraic operations gives

$$\rho_c = \frac{\rho_f}{1 + [(k\rho_f/\rho_o) - 1]e^{-\frac{V_r kt}{V}}} \tag{7}$$

where $\rho_c$, $\rho_f$ and $\rho_o$ are, respectively, the resistivity of the material added to the crystal lattice, of the feed-in material, and of the material used for loading the crucible.

An inspection of Eq. (7) indicates directly that for all values of other constants, if $\rho_f = \rho_o/k$, $\rho_c$ is independent of $t$ and is equal to $\rho_f$, but that if $\rho_f \neq \rho_o/k$, the value of $\rho_c$ approaches $\rho_f$ only when $t$ becomes very large.

Furthermore, Eq. (7) makes possible the calculation of the value of $\rho_o$ required for any desired resistivity (below 10 ohm-cm) of the single-crystal material grown, and also the variation in this resistivity with length grown, for cases where the resistivity of the feed-in rod, $\rho_f$, differs from the resistivity desired for the single-crystal material.

At $t = 0$, Eq. (7) reduces to $\rho_c = \rho_o/k$. Therefore, if a donor element for which $k = 0.005$, is used for preparation of n-type germanium, it follows that the value of $\rho_o$ to use for any particular $\rho_c$ may be determined by the simple relation: $\rho_o = 0.005 \rho_c$. If single-crystal material having a resistivity of 2 ohm-centimeters is desired, for instance, intrinsic germanium doped with this donor element to reach a resistivity of 0.01 ohm-centimeter must be used for the crucible melt.

The change with time of the resistivity of the germanium added to the lattice of the growing single crystal may be calculated from Eq. (7) by insertion of the numerical values for the constants involved. For a typical set of operating conditions, these are:

| | |
|---|---|
| $k = 0.005$ | Distribution coefficient of donor element in germanium. |
| $V_r = 0.314$ cm$^3$/min. | Corresponding to a single crystal 2 centimeters in diameter and of feed-in bar, and a rate of feed-in equal to the rate of crystal growth = 0.1 centimeter per minute. |
| $V = 70$ cm$^3$ | Volume of melt in boat. |
| $\rho_o = 0.01$ ohm-cm | |

Eq. (7) thus becomes:

$$\rho_c = \frac{\rho_f}{1 + (0.5 \rho_f - 1)e^{-0.0000224t}} \text{ ohm-cm} \tag{8}$$

It follows from an inspection of this equation that, for values of $t < 1000$ minutes $e^{-0.0000224}$ is very nearly equal to 1, and that $\rho_c$ is equal to 2 ohm-centimeters and is, for practical purposes independent of $\rho_f$ for values of this parameter greater than 2 ohm-centimeters. For $\rho_f = 40$ ohm-centimeters, for instance, $\rho_c$ calculated from Eq. (8) is equal to 2.06 a

t = 1000 minutes. It is possible, therefore, by feeding in intrinsic or near-intrinsic germanium, to draw from doped melt a total length of single crystal 2 centimeters in diameter equal to 100 centimeters before an appreciable increase in resistivity occurs.

In Fig. 4, a curve calculated from Eq. (7) is compared with experimental data. In spite of the fact that the determinations of $n_o$ and k are subject to error, and that maintaining V and $V_r$ constant is difficult during operating conditions, the correlation is good. Although near-intrinsic germanium was fed in during the growth of the crystal, its resistivity as shown by the data did not increase with time.
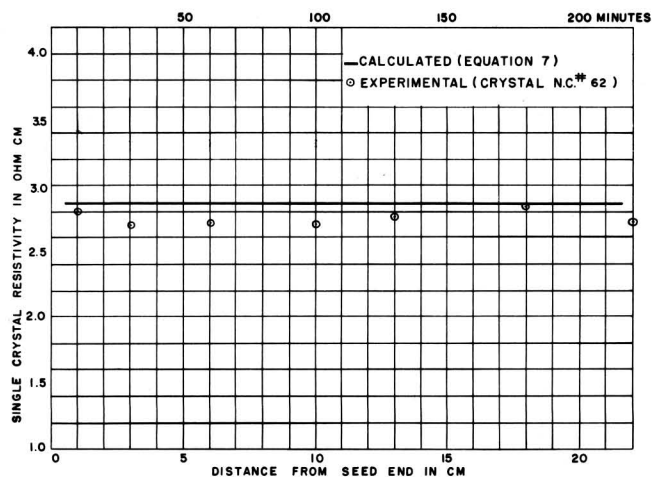


Fig. 4 – Variation in resistivity along length of continuous process crystal.

Results similar to those indicated above may be obtained when other doping agents are used, if the values of k for these impurities are of the same order of magnitude. As a consideration of Eq. (8) shows, $\bar{t}$, the length of time of growth before a noticeable increase (about 3%) in resistivity occurs as a result of feed-in of near-intrinsic germanium, varies with k, as indicated by the relation

$$\bar{t} = \frac{5}{k} \text{ minute}$$

If indium, k = 0.001, is used, for instance, for the preparation of p-type germanium, $\bar{t}$ = 5000 minutes. With regard to the above relation as well as with regard to prior equations involving the distribution coefficient k, a word of caution is in order. If crystal growth

occurs under conditions at which a pile-up of impurities occurs in the growth region of the melt, as a result of insufficient agitation or of rapid solidification, an effective rather than true value of k must be used. This effective value can, of course, be empirically determined for any particular condition of growth.

**Discussion**

Two single-crystal growing apparatuses of the type described above have been operated under laboratory conditions for an extended period. Though the operation of these furnaces has not been trouble-free, it has led to the production of several kilograms of single-crystal germanium of satisfactory quality for transistors. By the use of single-crystal seeds of different orientation, crystals as heavy as 400 grams have been grown in different crystal directions, especially in the 100, the 110, and the 111 direction. Growth in the 111 direction appeared most trouble-free and, consequently a large majority of the crystals produced were grown in that direction.

Some early difficulties were: melt-solidification at edge of the boat crucible during crystal growth, twinning, and non-uniform distribution of impurities throughout the single-crystal lattice. The first of these difficulties, melt-solidification, occurred as a result of the presence of "cold spots" at the ends of the graphite boat which "saw" the relatively cold end-caps of the Vycor furnace tubes. To minimize these "cold spots" and to eliminate their adverse effects, the following measures were taken:

1. Introduction of heat shields between the ends of the graphite boat and the ends of the furnace tube.
2. Cutting of a slot in the furnace brick directly above the center of the graphite boat to eliminate or reduce temperature gradient from middle to ends of boat.
3. Use of Globars having longer hot sections, and the placing of these closer to furnace tube.

By resorting to the above measures, it was found that the melt-solidification difficulty could be eliminated but that a higher incidence

of twinning in the growing crystal resulted. Apparently the increase in temperature gradient from the center of the melt to the hotter pot-rim, which led to the elimination of one difficulty, was a factor in bringing about the presence of another. The two upper Globars were, therefore, placed slightly higher with respect to the melt surface, and provisions were made for greater conduction of heat away from the growth region of the melt through the single crystal. These changes resulted in a lower radial thermal gradient over the melt surfaces and a higher gradient in the very region of crystal growth, and brought about reduction in the incidence of twinning to the point at which successive crystals could be produced without twin formation.

In connection with work done to modify the thermal gradients in the furnace, the observation was made that the degree of inhomogeneity in the distribution of impurities in the crystal lattice was greatly affected by these modifications. When in early work with the furnaces a relatively high thermal gradient existed between center and ends of the graphite boat, and when the crystals were grown at a low rate of rotation, 1 rpm, a cyclical variation in resistivity (striations) occurred along the length of the crystal.[3] Since crystal growth is more rapid at the relatively cool side of the melt, rejection of impurities by the growing lattice tends to be diminished due to "pile-up" of rejected impurities in this region. Lower resistivity material is, therefore, added to the lattice on the "cool" rather than on the "hot" side where the crystal growth is lower and less increase in concentration of impurities occurs. To eliminate or minimize this non-uniformity in impurity distribution, the rate of crystal rotation was increased to 60 rpm to effect better mixing. As a consequence, the striation-type of inhomogeneity was greatly reduced.

The observation was also made that the thermal gradient conditions, which led to melt-solidification when "cold spot" regions existed in the furnace, led to spurious resistivity variations along the length of the single crystal and also along its cross-section diameter, even at a high rate of rotation of the growing crystal. These types of non-uniformities were found to be greatly minimized after the modifications to optimize thermal

gradient conditions in the furnace were effected. Before-and-after results are shown in Fig. 5.
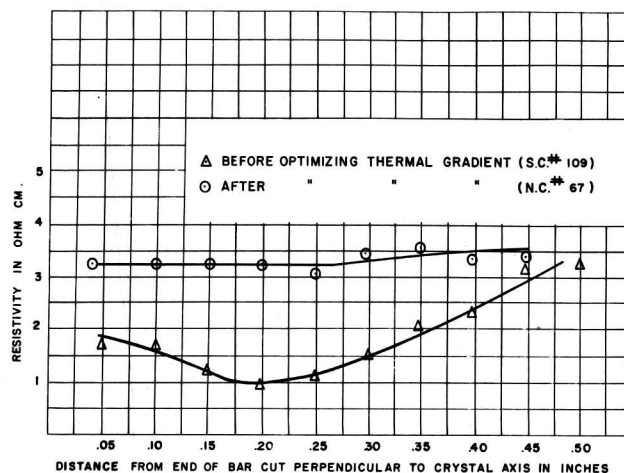


Fig. 5 – Radial variation in resistivity of continuous process crystal.

The work done to optimize thermal gradients in the furnace was carried out on a qualitative rather than on a quantitative basis, and the above paragraphs should be interpreted accordingly.

With regard to the rate of single-crystal "pull-out", higher rates than 1 millimeter per minute have been used experimentally but sometimes led to exaggerated melt-solidification and twinning difficulties, and have therefore been temporarily abandoned. It appears, however, that optimization of thermal gradients in the furnace will make higher rates of crystal "pull-out" practical.

As has been suggested, the close control of the temperature of the germanium melt is important for the maintenance of optimum operating conditions. A very small change in the temperature (1 or 2°C) of the growing crystal surface will materially affect the rate of growth and upset the desired equilibrium conditions. For this reason manual control of the temperature was used to supplement automatic control furnished by a voltage regulator and a Wheelco temperature regulator. Since supplementary manual temperature control was needed only because of the change in the temperature loss which occurs as the growing crystal is gradually pulled away from the melt surface, it follows that proper programming of the temperature regulation can effectively replace supplementary manual control.

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[3] LB-896, *Resistivity Striations in Single-Crystal Germanium.*

Herbert Nelson
Herbert Nelson